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CORROSION OF ALUMINUM ALLOYS

The fundamental mechanisms of the corrosion of aluminum alloys in water at 200 to 300 C (390 to 570 F) are being studied at Oak Ridge.⁽¹⁾ Alloy additions included zinc, magnesium, copper, iron, yttrium, and beryllium. Within certain concentration ranges, all additives greatly improved the corrosion resistance of aluminum. The marked improvement occurred when a second phase was present. No electrochemical effect could be ascribed to the second phase because the observed reduction in corrosion rate of the several alloys was independent of whether the second phase was anodic or cathodic to the aluminum matrix.

The movement of ions through the passive film on aluminum has been investigated in Norway.⁽²⁾ In room-temperature, high-purity water, passivation was found to be due to a thin barrier film 10 to 30 Å thick adjacent to the metal surface. The barrier film was an ionic semiconductor in which the transport of both anions and cations determined the corrosion rate. The barrier oxide was found to be unstable in water and was continuously converted to the hydrated bulk oxide. It was concluded that the bulk oxide also was important in the corrosion process because it protected the barrier oxide from the water.

Corrosion behavior and surface treatments to prevent corrosion are among the subjects covered in the data handbooks for aluminum alloy 2219 and Inconel Alloy 718 recently compiled by Syracuse University.^(3,4)

CORROSION OF FERROUS ALLOYS

High-Strength Steels. The effect of notches and salt-water corrosion on the flexural fatigue strength of HT, HY-80, HY-100, HY-130/150, and Marage 180 steels has been studied at the Marine Engineering Laboratory.⁽⁵⁾ It was found that both mechanical notches and salt-water corrosion were more damaging in high-cycle than in low-cycle fatigue. The combined effect of mechanical notches and salt water was greater than either separately. The critical notch-root radius for HT, HY-100, and, presumably, HY-80, was approximately 0.010 in., while the critical radius for HY-130/150 and Marage 180 was at, or less than, 0.002 inches. The high-cycle, salt-water corrosion-fatigue strengths of the sharply notched steels were less than 10,000 psi beyond 10-million cycles, regardless of tensile yield strength.

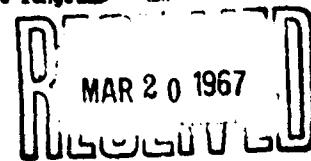
The effect of chemical milling on susceptibility to hydrogen embrittlement of high-strength steels H-11, 4340, Vascojet 1000, and 17-7 PH has been studied at the Naval Air Engineering Center.⁽⁶⁾ Results indicated that the acid baths used for chemical milling initially embrittle all of these alloys except 4340, but that recovery of ductility occurs within 1 week at room temperature if there is no barrier to the escape of hydrogen (such as plating). Chemical milling increased the susceptibility to stress-corrosion cracking in tests conducted with H-11 and 17-7 PH in 3.5 percent NaCl solution.

The susceptibility of hardened steel to hydrogen embrittlement in black oxide and zinc phosphating processes has been studied at Rock Island Arsenal.⁽⁷⁾ After the coating treatment, notched tensile bars of 1045, 1095, and 4140 steels hardened to Rockwell C 50 were loaded to 75 percent of the ultimate notched tensile strength. The black oxide treatment produced no embrittlement, but the phosphate treatment caused severe hydrogen embrittlement. Baking at 210 F for 24 hours was not sufficient to consistently eliminate the embrittling effects resulting from the phosphate treatment.

STAINLESS STEELS

Conceptual sketches illustrating the theory of initiation of stress-corrosion cracking in stainless steels and other alloys have been prepared by the Ohio State University.⁽⁸⁾ The theory presumes that cracks initiate at anodic sites where active slip planes under applied stress emerge at the surface and rupture the passive oxide film. This mechanism is used to explain the improved resistance to cracking obtained by preoxidizing a specimen prior to exposure to a crack-producing environment over that obtained by exposing the specimen directly to the environment.

The factors affecting the critical potential below which pitting of 18Cr-8Ni stainless steel does not occur in aqueous chloride solutions have been studied at the Massachusetts Institute of Technology.⁽⁹⁾ It was found that increasing the chloride-ion concentration shifted the critical potential to more active values, while the presence of other ions, such as ClO_4^- , SO_4^{2-} , NO_3^- , or OH^- , shifted the potential to a more noble value. Sufficient concentrations of these other ions inhibited pitting. The critical potential in chloride solutions was not affected appreciably in the acid range, but moved markedly in the noble direction in the alkaline range.



CORROSION OF NICKEL- AND COBALT-BASE ALLOYS

Exhaust Gases. Inconel "X", Rene 41, and Hastelloy have been exposed to hot exhaust gases from combustion of oxygen-hydrogen in mixture ratios of 75 to 150 in research conducted at the NASA-Marshall Space Flight Center.⁽¹⁰⁾ Firings were conducted for 30 seconds in a 3600-pound-thrust combustor at a chamber pressure of 1000 psia. There was no erosion or melting of these materials except during a mixture ratio shift through stoichiometry in the start transient of one firing.

Avco has undertaken a study of sulfidation corrosion of 12 superalloys in JP-4R fuel exhaust gases containing synthetic sea salt.⁽¹¹⁾ Initial results of cyclic tests producing 120 total hours at temperature have indicated no sulfidation of a cobalt-base alloy (X-40) at temperatures to 1750 F. The 11 nickel-base alloys exhibited varying degrees of sulfidation. In general, this localized penetration was first detected at about 1450 F, reached a maximum depth of as much as 20 mils at about 1575 F, and was no longer evident at about 1750 F.

On the other hand, studies at Allison with sodium sulfate and several of these same superalloys have shown a definite increase in corrosion and sulfidation with increasing temperature in the range of 1700 to 1900 F.⁽¹²⁾ Tests runs were of 500-cycle duration. A cycle consisted of a 0.5-minute spray of 1 percent sodium-sulfate solution between 1.5-minute heating periods.

Hot N_2O_4 . The oxidation of refractory metals and Alloy 718 in flowing N_2O_4 at 1200 F has been studied by Marquardt.⁽¹³⁾ Thirty-minute runs produced some discoloration but little weight gain on the Alloy 718 and B-66 columbium alloy. Heavy oxide buildup occurred on unalloyed columbium, C-103 columbium alloy, and unalloyed tantalum. The oxide spalled on the latter two materials.

Water and Steam. The current status of stress-corrosion cracking in high-nickel alloys has been reported by Coriou, et al.⁽¹⁴⁾ Intergranular cracking was observed in stressed Inconel 600 and Hastelloy Alloy B exposed to high-purity water at 662 F and in stressed Inconel 600 exposed to 1112 F steam. The behavior under these conditions was compared with the high susceptibility of these alloys to intergranular attack in boiling nitric acid containing Cr^{+6} ions. An earlier paper by the International Nickel Company has shown that Inconel 600 (and Type 304 stainless steel) exhibited intergranular cracking in high-temperature, high-purity water when there were crevices at the highly stressed areas and the water contained oxygen.⁽¹⁵⁾ Lead contamination in high-temperature water also was found to cause stress-corrosion cracking of Inconel-600.

The account of stress-corrosion cracking of highly stressed Inconel 600 tubes in the Agesta Nuclear Power Station has been published by Swedish scientists.^(16,17) The cracks originated on the outside surface, which contacted light water at pH 10 (LiOH or KOH) and 217 C (423 F) for some 150 days. Cracks were found in crevices and on fully exposed surfaces. Surface contamination at the cracks was found to be limited to $1 \mu g/cm^2$ fluorine. Subsequent laboratory tests in high-purity water and in

1M LiOH at 220 C (428 F) failed to produce cracks in stressed Inconel 600 samples. Although the cause of cracking was not established, it was recommended that Inconel 600 be vacuum melted to minimize impurities, particularly carbon, that fabrication and operation stresses be minimized, and that crevices and localized boiling be eliminated in the reactor.

Evaporation. Evaporation rates of superalloys Hastelloy Alloy X and Hanes Alloy 25 in helium have been studied at Battelle-Northwest.⁽¹⁸⁾ Preliminary results indicate that evaporation rates increase with temperature (2000 to 2100 F) and with velocity above 300 ft/sec. Maximum metal evaporation rates were about 0.07 mils/day.

Seawater. The results of a 1-year galvanic corrosion test in seawater flowing at 2 fps have been reported by the Naval Marine Engineering Laboratory.⁽¹⁹⁾ The following alloys were not subject to galvanic corrosion when coupled to Monel: Stellite 6K, -6B, and -9BM2, Tantalum G, Cobenium, and Kennametal K601. Galvanic corrosion was observed on the following alloys when coupled to Monel: Stellite 3 and Star J, Kennametal K162B, K82, K96, K701, and K801, and Bismuth Metal.

CORROSION OF TITANIUM

General. Information obtained since 1960 on the corrosion behavior of titanium and its alloys has been reviewed by the Defense Metals Information Center.⁽²⁰⁾ Included among the environments were salts, mineral acids, gases, liquid metals, and organic compounds. Considerable attention was given to the problem of stress-corrosion cracking.

Stress-Corrosion Cracking. The Titanium Metals Corporation of America has shown that Ti-6Al-4V alloy does not stress-corrosion crack in reagent-grade isopropyl alcohol alone or containing 2 g/l HCl or NaCl.⁽²¹⁾ Notched and unnotched bent-beam specimens were exposed 5 days at stresses up to the yield strength. Similar tests in methyl alcohol produced stress-corrosion cracking.

The effect of thermal cycling to simulate service conditions on the hot-salt (NaCl) stress-corrosion-cracking behavior of titanium alloys is being studied at Northrop Norair.⁽²²⁾ Cyclic exposures at 650 F equivalent to nearly 10 times the continuous stress-corrosion-cracking nucleation time have not produced stress-corrosion cracking in Ti-6Al-4V or Ti-13V-11Cr-3Al alloys. In addition, cyclic exposures at 650 F suppressed growth rates of existing stress-corrosion cracks and the nucleation of new cracks in Ti-8Al-1Mo-1V alloy. The thermal cycle consisted of heating to 650 F in 10 to 15 minutes, holding at 650 F for 3 hours, cooling in 45 to 50 minutes. Continuous exposure at 450 F produced hot-salt stress-corrosion cracking in Ti-8Al-1Mo-1V stressed at 95 ksi.

The corrosion behavior of welded alpha-beta titanium alloys for application to submarine hull plate has been reported by Titanium Metals Corporation of America.⁽²³⁾ The alloys were Ti-6Al-4V, Ti-6Al-2Mo, Ti-4Al-0.3Mo, and Ti-7Al-2.3Mo. Circular-weld-patch-type restraint tests showed no evidence of weld-zone cracking in air or in syn-

thetic seawater. Slow bend tests on small Charpy-impact specimens with 0.001-inch machined radius in the notch area revealed that only the Ti-4Al-0.2Mo alloy failed at lower sustained loads in seawater than in air.

The effect of fuel-tank sealants on the stress-corrosion cracking of titanium alloys at 450 to 600 F has been studied by TRW Equipment Laboratory.⁽²⁴⁾ Current results indicate that Du Pont polyimide varnish (RK692) produced no delayed failures in pre-cracked specimens at temperatures to 600 F and stresses to 95 percent of the notch tensile yield strength. AFML triazine sealant promoted extensive delayed failure in relatively short times, while performance in Dow Corning fluorosilicone elastomer (Q94-002) was intermediate between that in the varnish and the triazine sealant. Ti-13V-11Cr-3Al alloy was more susceptible to delayed failure than Ti-6Al-4V or Ti-8Al-1Mo-1V alloys.

Titanium alloys have been cathodically charged with tritium by Douglas Astropower in connection with stress-corrosion-cracking studies.⁽²⁵⁾ Autoradiographs showed that tritium introduced by cathodic charging in tritiated water was distributed uniformly throughout the lattice of the Ti-5Al-2.5Sn alloy. However, no tritium was found at hydride platelets that formed in the microstructure of this alloy. In the Ti-6Al-4V alloy, tritium was evenly distributed in the alpha lattice at low charging-current densities, but appeared to concentrate in alpha-beta and alpha-alpha boundaries at high current densities. No tritium was found in the beta phase of the Ti-6Al-4V alloy or in the all-beta Ti-13V-11Cr-3Al alloy.

CORROSION OF REFRACTORY ALLOYS

Lewis Research Center has screened 57 materials for throat inserts for ablative-material nozzle sections.⁽²⁶⁾ The propellant was N_2O_4 and 50:50 hydrazine: unsymmetrical dimethylhydrazine. Engine conditions were 100 psia chamber pressure with an oxidizer-fuel ratio of 2.0. Rapid oxidation was experienced with the refractory metals tantalum and molybdenum and several of their alloys. Optimum performance was obtained with pyrolytic silicon carbide coating on graphite which withstood four test cycles totalling 722 seconds before failure.

CORROSION OF BERYLLIUM

The corrosion of beryllium in seawater has been reported by the Air Force Institute of Technology.⁽²⁷⁾ Results of 14-day tests in aerated seawater at 90 F revealed a corrosion rate of 25.9 mils/yr and pitting to a maximum depth of 15 mils. Transgranular stress-corrosion cracking was observed in 59 F seawater at stress levels of less than one-half the yield strength.

COATINGS

The results of 21 months' exposure in tropical Panama of 28 paint systems on steel have been reported by the Army Coating and Chemical Laboratory.⁽²⁷⁾ Specimens were exposed at breakwater, in an open field, and in a rain forest. It was found that no single system offered optimum corrosion protection under all exposure conditions. At the breakwater

site, the best paint system was zinc phosphate-phenolic primer-phenolic enamel, which corroded least at score marks. At the other sites, numerous other systems performed equally well or better.

Lockheed has made a corrosion-control study of the SQA Agena vehicle.⁽²⁸⁾ The corrosion problems were found to arise primarily from the inadequacy of existing coating systems on magnesium and from inadequate methods of protecting removable mating surfaces.

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